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Experimental resonant two-photon study of the lowest confined exciton fine structure in CuCl quantum dots

A. V. Baranov†§, S. Yamauchi†, Y. Masumoto† and A. V. Fedorov§
† Institute of Physics, University of Tsukuba, Tsukuba, Ibaraki 305, Japan
§ Vavilov State Optical Institute, St. Petersburg, 199034, Russia

Abstract. Fine structure of low-energy confined exciton in CuCl spherical nanocrystals has been studied by a resonant size-selective two-photon-excited luminescence (TPL) spectroscopy with high spectral resolution. A band of resonance luminescence (RL) arising due to annihilation of the lowest-energy exciton and its LO-phonon replica were observed to be doublets. Analysis has shown that the components of the doublets connect with the pair of exciton states which have been attributed to low-energy confined states (1S) of two transversal excitons (T_1 and T_2) split by the size-dependent spin-orbit interaction. The physical reason of the splitting is similar to removing of Kramers degeneration of electron states in the bulk crystals of T_d symmetry.

Fine structure of optical spectra near band edge absorption and luminescence of quantum dots (QD's) is of great interest since it gives ones information about low-energy confined electrons (excitons), confined phonons, and interactions between them as well as symmetries of the quasi-particle states and selection rules of optical and phonon-assistant transitions. Fine spectral structure caused by a short-range and long-range exchange interactions ("dark" and "bright" electron-hole pair states [1], and "longitudinal" and "transversal" confined excitons states [2], respectively) have been observed as well as induced by exciton-phonon interactions (exciton-acoustic-phonon [3] and polaron [4] states).

An additional fine structure induced by spin-orbit interaction in crystals of T_d symmetry has not been considered for QD's systems so far. In such crystals [5], conduction and valence bands have fine structure near the Brillouin zone center due to spin-orbit interaction removing the Kramers degeneracy of electron states with nonzero wave vector. Obviously that the splitting of electron states results in a splitting of the transversal exciton on two states T_1 and T_2. A value of the T_1–T_2 splitting is proportional to $|\mathbf{k}|^3$ for excitons involving hole from the spin-orbit-split valence band ($\mathbf{k}$ is the electron (hole) wave-vector). Although theory of this effect for QD's is yet to be developed, from general point of view it is reasonable to suppose that the T_1–T_2 splitting for QD's should be proportional to R^{-3}, where R is the QD radius. It follows from effective mass approximation where size-dependences of physical parameters of spherical QD's can be obtained by a replacing of wave-vector modulus of quasi-particles with quantity proportional to $1/R$.

We report the high-resolution size-selective TPL spectroscopy of CuCl spherical nanocrystals where T_1–T_2 splitting seems to contribute importantly to the fine spectral structure. The resonant TPL spectroscopy of quantum dot systems presents with the important advantages to investigate a fine structure of low-energy quasi-particle states since an incident light does not practically mask features with small Stokes shifts in secondary radiation spectra at two-photon excitation [2].

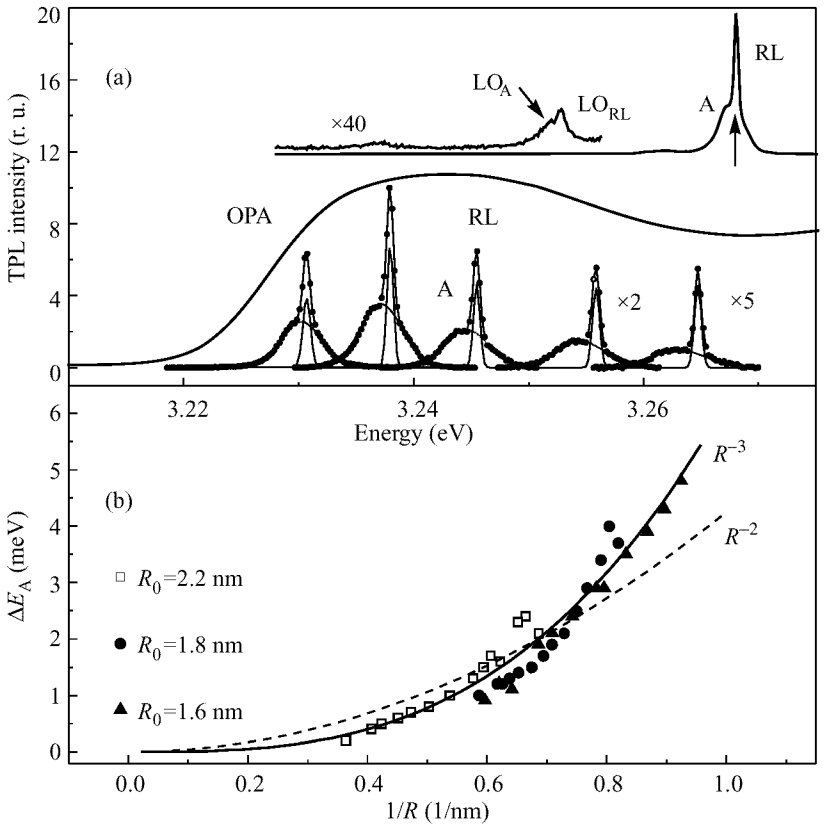

Fig 1.

CuCl QD's embedded in a glass matrix have been studied at 2 K. Dot's radii were in range from 2.5 to 1.2 nm. TPL was excited by a wavelength tunable Ti:sapphire laser pumped by a 3 kHz Q-switch YAG:Nd^{+3} laser. The emitted light was analyzed with spectral resolution of 0.5 meV ($\sim$ 4 cm^{-1}). For temporal analysis TPL was excited by a 2 ps Ti:sapphire laser pulse radiation; a time resolution of 150–200 ps was adopted.

Inset in Fig. 1(a) shows an example of size-selective TPL spectrum resonantly excited within inhomogeneously broadened one-photon absorption (OPA) band of Z_3 exciton for the specimen with a QD's mean radius, R_0 of 2.2 nm. The fine doublet structure with energy about twice energy of the incident photons, $2E_i$ (shown by an arrow) is clearly seen in detail in Fig. 1(a) where the doublets are shown for different $2E_i$. So, a narrow RL band of energy equal to $E_{RL} = 2E_i \equiv E_{1S}$, where E_{1S} is the energy of the lowest-energy confined exciton state, have been found having a broad satellite (A-band) with Stokes shift increasing up to $\sim$ 4.8 meV with increase of $2E_i$, or decrease of the nanocrystal size. The TPL spectra of specimens with $R_0 = 1.8$ and 1.6 nm show the same RL–A doublets. Analogous doublet structure consisting from narrow (LO_{RL}) and broad (LO_A) bands can be seen in the region of LO-phonon replicas of the RL and A bands (inset in Fig. 1(a)) with Stokes shifts of 25.8 meV, respectively.

Main experimental results are summarized as follows:

1. Spectral width of the RL band was found to be limited by the laser line one of

0.6 meV and much smaller than the A-band width of 3.5–4.5 meV. Ratio of spectral widths of the LO_A and LO_{RL} bands is about 4–5;

2. Stokes shift of the A-band ($\Delta E_A = E_{RL} - E_A$) increases from 0.4–0.5 meV to 4.8 meV with decrease of the nanocrystal radius: ΔE_A as a function of $1/R$ is presented in Fig. 1(b). It is seen that $\Delta E_A(R)$ demonstrates clear deviation from R^{-1} dependence and allows approximation by rather R^{-3} function than R^{-2} one.

3. The RL excitation spectrum (ES) shows a resonant enhancement in the energy region corresponding to a direct two-photon generation of the 1S confined Z_3 exciton and reflects a size distribution of the nanocrystals [2]. Maximum of ES of the A-band coincides with that of the RL band. It means [2] that A-band arises due to direct two-photon excitation either the 1S exciton state or some exciton state with energy slightly more than 1S exciton energy. Due to broad size distribution we can not distinguish these cases by comparison of the ES positions. Integral intensity of the A-band is about four times more than that of RL at maximum of the corresponding ES.

4. Time decay measurements of TPL excited at ES maximum and measured in the regions of $2E_i$ and $2E_i - E_{LO}$, where E_{LO} is the LO phonon energy, showed that decay times of the RL and A bands, and their LO-phonon replicas have the same value of about 0.6 ns. It shows that the lines considered more likely start from the same confined exciton state.

5. The RL and A bands have the same degree of linear polarization; it gives additional evidence that both the RL and A bands arises due to radiative annihilation of the same exciton state.

RL behaviors give evidence that it is resonance luminescence starting from the relatively long-living lowest energy confined exciton state. Then, the LO_{RL} band results from the LO-phonon-assistant radiative annihilation of the same state.

The A-band and its LO-phonon replica (LO_A) in turn can arise due to a fine structure of low-energy confined exciton states. Indeed, our experimental data give evidence that the RL–A and LO_{RL}–LO_A doublets are most likely caused by a fine structure of lowest energy 1S exciton states, namely, the $1S_{T1}$ and $1S_{T2}$ states of two transversal excitons (T_1 and T_2) split by the size-depended spin-orbit interaction. Then, the RL band and its LO-phonon replica come from two-photon excitation of the lowest energy $1S_{T1}$ exciton and its phononless and phonon-assistant radiative annihilation. At the same incident photon energy the A band and its LO-phonon replica arise from nanocrystals of larger size due to two-photon generation of the excitons in the $1S_{T2}$ state with energy of 0.4–4.8 meV more than the $1S_{T1}$ state, subsequent nonradiative transition to the $1S_{T1}$ state, and its phononless and phonon-assistant radiative annihilation.

Note that short-range exchange interaction can not be responsible for the doublets because a singlet-triplet exciton splitting for the nanocrystals has to be equal or more than that for the bulk CuCl (2.6 meV). The same reason allows ones to exclude from considerations the "longitudinal" exciton state because corresponding L–T splitting has much more values [2] than those observed for the RL–A doublet.

The essentially higher spectral width of the A-band than that of the RL band is easily understandable in framework of our scheme where the $1S_{T2}$ state is supposed to be homogeneously broadened in large part due to fast nonradiative transitions to the $1S_{T1}$ state. In such a situation, the $1S_{T2}$ excitons are simultaneously generated in nanocrystals of more broad range of sizes than the $1S_{T1}$ excitons. For each of the nanocrystals from this ensemble the narrow TPL line due to annihilation of the $1S_{T1}$ exciton created by

transitions from $1S_{T2}$ state contributes to the A-band. Since the annihilation energy is size-dependent, the A-band is envelope contour of the TPL bands with homogeneous widths equal to the RL line width. Simultaneous excitation of relatively large number of nanocrystals results also in relatively large integral intensity of the A-band. Note, the same reasons explain the difference between the LO_A and LO_{RL} band widths and intensities. Evidently that the decay times of the PL, A, LO_A, and LO_{RL} bands thus considered should be approximately the same as well as their polarization properties that satisfies to our findings.

The assignment of the A-band to both the exciton-acoustic-phonon state and acoustic-phonon-assistant luminescence looks also rather unlikely because of clear distinction of $\Delta E_A(R)$ from expected R^{-1} dependence. The reasons why the signal of the acoustic-phonon-assistant processes is rather weak in TPL spectra of our samples are not quite clear to us. Probably the A band contains a small contribution of the acoustic phonon signal undistinguished due to strong overlapping of two bands of different origin.

As far the observed ΔE_A size dependence, it is expected for our model of the T_1–T_2 splitting of Z_3 confined exciton in the CuCl quantum dots. Really, the experimental size-dependence of $\Delta E_A(R)$ [Fig. 1(b)] can be well fitted by the R^{-3} function.

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